
Chapter 5

Hydrogen Sulfide in Sewer

Introduction

Sanitary wastewater solids deposited in combined sewers (CS) systems during dry weather is a major contributor to the CSO-pollution load. Furthermore, sulfates are released from organic substances contained in the sewer sediments by bacteria under anaerobic conditions. In the absence of dissolved oxygen and nitrates, sulfates serve as electron acceptors and are chemically reduced to sulfides and to H_2S by bacteria. The hydrogen sulfide is then converted to sulfuric acid, which disintegrates sewer pipes. Thus, dry weather sewer sediments create odor and sewer decomposition problems in addition to the CSO pollution (Fan et al., 2001).

The production and release of H_2S gas in municipal wastewater collection systems is responsible for numerous odor complaints and the destruction of sewer pipes and other wastewater facilities. The process begins with the biological reduction of sulfate to sulfide by the anaerobic slime layer residing below the water surface in wastewater collection systems. The anaerobic bacteria utilize the oxygen in the sulfate ion as an electron acceptor in their metabolic processes. The resulting sulfide ion is transformed into H_2S gas after picking up two hydrogen ions from wastewater. Once released to the sewer atmosphere, an aerobic bacteria (*Thiobacillus*) which resides on sewer walls and surfaces above the water line consume the H_2S gas and secrete sulfuric acid. In severe instances, the pH of the pipe can reach as low as 0.5. This causes severe damage to unprotected collection system surfaces and can eventually result in the total failure of the sewer piping and the uncontrolled release of raw wastewater to the environment.

This chapter describes detailed procedures and methods for conducting field sampling and monitoring procedures to determine transient levels of H_2S generation of agitated beds within the presence of oxygen during simulated storm conditions.

Background

For domestic wastewater the main source of sulfide (S^{2-}) is sulfate (SO_4^{2-}). Sulfide generation is a bacterially mediated process occurring in the submerged portion of combined and sanitary sewers and force mains. Fresh domestic wastewater entering a collection system is usually free of S^{2-} . However, a dissolved form of S^{2-} soon appears as a result of low dissolved oxygen content; high-strength wastewater; low flow velocity and long detention time in the collection system; elevated wastewater temperature; and extensive pumping. The chemistry of sulfur cycle, microbial process in sewer networks, and mechanisms of corrosion are covered elsewhere (Thistlethwayte 1972; U.S. EPA, 1985; Hvitved-Jacobsen 2002). This section briefly discusses the relationship of SO_4^{2-} reduction, biochemical oxidation, and the factors affecting those biotransformations in sewer.

Once released from the wastewater as H_2S gas, odor and corrosion problems begin. Another type of bacteria utilizes H_2S gas to produce H_2SO_4 that causes the destruction of wastewater piping and facilities. Operation and maintenance (O&M) expenditures are required to correct the resulting damage caused by this H_2SO_4 . In severe instances, pipe failure, disruption of service and uncontrolled releases of wastewater can occur.

The first step in this bacterially mediated process is the establishment of a slime layer below the water level in a sewer. This slime layer is composed of bacteria and inert solids held together by a biologically secreted protein “glue” or film called Zooglea. When this biofilm becomes thick enough to prevent dissolved oxygen from penetrating it, an anoxic zone develops within it. Approximately two weeks is required to establish a fully productive slime layer or Zooglea film in pipes. Within this slime layer, sulfate reducing bacteria use the sulfate ion (SO_4^-), a common component of wastewater, as an oxygen source for the assimilation of organic matter in a way equivalent to dissolved oxygen is used by aerobic bacteria. Sulfate concentrations are almost never limiting in normal domestic wastewaters. When SO_4^- is utilized by these bacteria, S^- is the by-product. The rate at which S^- is produced by the slime layer depends on a variety of environmental conditions including the concentration of organic food source or biochemical oxygen demand (BOD), dissolved oxygen concentration, temperature, wastewater velocity, and the area of the normally wetted surface of the pipe.

As SO_4^- is consumed, the S^- by-product is released back into the wastewater stream where it immediately establishes a dynamic chemical equilibrium between four forms of sulfide; the sulfide ion (S^-), the bisulfide or hydrosulfide ion (HS^-), dissolved H_2S ($\text{H}_2\text{S}_{(\text{aq})}$), and H_2S gas ($\text{H}_2\text{S}_{(\text{g})}$). The rate at which H_2S leaves the aqueous phase is governed by Henry’s Law and other factors (Hvitved-Jacobsen, 2002).

Factors Affecting Sulfide Concentration

Settleable Solids.

Periods of low flow in the collection system correlate to lower average wastewater velocities. Low-flow velocities allow material, usually grit, to settle in the collection system piping. This increases the mass and surface area of material in the collection system upon which SO_4^- reducing bacteria (slime layer) can grow, and can lead to an increased conversion of SO_4^- to S^- . The interaction between a large quantity of bacteria and an almost unlimited food source will create dissolved S^- spikes that are subsequently released in areas of high turbulence. This trend is common and well documented in many cities with similar grit deposition problems such as Boston, Los Angeles, St. Louis, and Houston (US EPA 1985).

Temperature.

Higher wastewater temperatures increase the metabolic activity of the SO_4^- -reducing organisms, causing faster conversion of SO_4^- to S^- and increased dissolved S^- concentrations. It has been estimated that each incremental 7°C (12.5°F) increase in wastewater temperature doubles the production of S^- (Fan et al., 2001).

Flow Turbulence.

Turbulence is a critical parameter in controlling $\text{H}_2\text{S}_{(\text{g})}$ release from wastewater. The effects of $\text{H}_2\text{S}_{(\text{g})}$ odor and corrosion are increased by orders of magnitude at points of turbulence. Henry’s law governs the concentration of gas over a liquid containing the dissolved form of the gas. Any action that serves to increase the surface area of the liquid also increases the driving force from the liquid to the gas phase. Thus, structures causing turbulence should be identified and retrofitted to eliminate hydraulic jump, improve streamlining transmission, and reduce the subsequent $\text{H}_2\text{S}_{(\text{g})}$ releases. This same release mechanism is exhibited whenever wastewater containing dissolved sulfide is aerated.

Structural Corrosion

Thiobacillus aerobic bacteria, which commonly colonize pipe crowns, walls and other surfaces above the waterline in wastewater pipes and structures, have the ability to consume $\text{H}_2\text{S}_{(\text{g})}$ and oxidize it to H_2SO_4 . This

process can only take place where there is an adequate supply of $\text{H}_2\text{S}_{(\text{g})}$ ($> 2.0 \text{ ppm}_\text{v}$), high relative humidity, and atmospheric oxygen. These conditions exist in the most of wastewater collection systems for part of the year. A pH of 0.5 (approximately equivalent to a 70 mL/L of H_2SO_4 concentration) has been measured on surfaces exposed to severe $\text{H}_2\text{S}_{(\text{aq})}$ environments ($> 50 \text{ ppm}_\text{v}$ in air).

The effect of H_2SO_4 on concrete surfaces exposed to the sewer environment can be devastating. Sections of collection interceptors and entire pump stations have collapsed due to loss of structural stability from corrosion. The process of concrete corrosion, however, is a step by step process that can sometimes give misleading impressions. The following briefly describes the general process of concrete corrosion in the presence of a sewer atmosphere:

Freshly poured concrete has a pH of approximately 11 to 12, depending upon the composition of mixed aggregates. This high pH is the result of the formation of calcium hydroxide [$\text{Ca}(\text{OH})_2$] as a by-product of the hydration of cement. $\text{Ca}(\text{OH})_2$ is a very caustic crystalline compound that can occupy as much as 25% of the volume of concrete. A surface pH of 11 or 12 will not allow the growth of any bacteria; however, the pH of the concrete is slowly lowered over time by the affect of carbon dioxide (CO_2) and $\text{H}_2\text{S}_{(\text{g})}$. These gases are both known as “acid” gases because they form relatively weak acid solutions when dissolved in water. CO_2 produces carbonic acid and H_2S produces thiosulfuric and polythionic acid. These gases dissolve into the water on the moist surfaces above the wastewater flow and react with the $\text{Ca}(\text{OH})_2$ to reduce the surface pH. Eventually the surface pH is reduced to a level that can support the growth of bacteria (pH 9 to 9.5).

The time it takes to reduce the pH is a function of the concentration of CO_2 and $\text{H}_2\text{S}_{(\text{g})}$ in the sewer atmosphere. It can sometimes take years to lower the pH of concrete from 12 to 9, however, in severe situations it can be accomplished in a few months. Once the pH of the concrete is reduced to about pH 9, biological colonization can occur. More than 60 different species of bacteria are known to regularly colonize wastewater pipelines and structures above the water line. Most species of bacteria in the genus *Thiobacillus* have the unique ability to convert $\text{H}_2\text{S}_{(\text{g})}$ to H_2SO_4 in the presence of oxygen. Since the production of H_2SO_4 from H_2S is an aerobic biological process, it can only occur on surfaces exposed to atmospheric oxygen.

The color of corroded concrete surfaces can be various shades of yellow caused by the direct oxidation of H_2S to elemental sulfur. This only occurs where a continuous high concentration supply of atmospheric oxygen or other oxidants are available. The upper portions of manholes and junction boxes exposed to high H_2S concentrations are often yellow because of the higher oxygen content. This same phenomena can be observed around the outlets of odor scrubbers using hypochlorite solutions to treat high $\text{H}_2\text{S}_{(\text{g})}$ concentrations.

Another damaging effect of H_2SO_4 corrosion concrete is the formation of a mineral called “ettringite” calcium sulfbaluminate hydrate ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$) or gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) produced by the incomplete reaction H_2SO_4 and cement. It forms at the boundary line between the soft CaSO_4 layer and the sound, uncorroded concrete surface. Ettringite is damaging because it is an expansive compound that occupies more space than its constituents. When ettringite forms, it lifts the corroded concrete away from the sound concrete and causes a faster corrosion by continually exposing new surfaces to acid attack. Although the rate of concrete loss depends on a series of factors including ettringite formation, it is not uncommon to see concrete loss of 1 in. per yr in high sulfide environments.

Sampling and Monitoring

The control of H_2S in wastewater systems is of vital importance to the wastewater industry. The biological and chemical processes resulting in sulfide production in wastewater are well understood, but there are significant contributing factors about which we know nothing. Settled solids and other debris in sanitary sewers and wastewater collection systems provide a greatly increased surface area upon which anaerobic sulfate reducing bacterial slime can grow, thereby increasing the incremental (per ft) sulfide production potential of sewers.

Objective of Field Investigation

The objective of field investigation is to determine the change in concentration of dissolved H_2S . Subsequent reduction in $\text{H}_2\text{S}_{(\text{g})}$ can also be measured as a secondary objective. The field monitoring measures the sulfide production in a sewer containing moderate to heavy settled solids and debris, sample and characterize the solids in the sewer. An additional facet of the field investigation will measure in-situ dissolved sulfide concentrations inside the interstitial spaces of a typical debris pile in the sewer. From knowledge of the practical pore space volume and the surface area, the specific sulfide production rate can be determined. The mass of sulfide can be calculated, and H_2S could be prevented by cleaning the upstream sewers.

From an analytical standpoint, the primary objectives of field investigation are to determine the following:

- The mass of sulfide generated in-situ by a known type and quantity of debris
- The reduction of sulfide that can be achieved by removing sewer debris
- The sewer headspace H_2S concentrations of a clean and dirty sewer
- The odor and corrosion reduction achieved by removing sewer debris
- The ventilation dynamics of a sewer being flushed
- The approximate odor potential of flushing a debris laden sewer
- The effect of flushing on the downstream long-term corrosion potential

Hydrogen sulfide and Dissolved Sulfide Sampling and Testing Procedures

Hydrogen sulfide in the gas and dissolved phases are the focus of the field inspections. Hydrogen sulfide gas testing includes measuring H_2S gas concentration at the manholes upstream and downstream from the test area. Measurements can be taken at the manhole access points before, during and after flushing. Dissolved sulfide testing includes measuring dissolved sulfide ion concentration in the wastewater upstream and downstream from the test area and at specific points in between. Samples shall be collected before and after flushing. Additional dissolved sulfide ion measurements can be taken from the debris piles within the sewer, prior to flushing. These measurements are taken in-situ by a project engineer experienced in sulfide sampling and confined space entry (CSE). The following procedures shall be used to measure H_2S gas and dissolved sulfide ion concentration.

Air samples are analyzed for H_2S by three instruments equipped with an extension hose, H_2S gas detection tubes, and a H_2S gas detection and recording station. Liquid samples are analyzed using Gastec tubes for dissolved H_2S . Continuous dissolved H_2S sampling can be accomplished by an American Sigma Streamline model 800 SL (or equivalent) automatic portable liquid samplers.

The Industrial Scientific STX70 or TMX412 gas detector and recording station are used to continuously monitor the H_2S gas concentration in the sewer. The Industrial Scientific STX70 and TMX412 are small portable units enclosed in impact resistant case.

These instruments contain a passive H_2S electrochemical diffusion type sensor. The sensor signal is monitored on a single channel in the range of 0 to 999 ppm at 1 ppm increments. The data is displayed on the LCD digital display and recorded into memory by the data logger according to preconfigured parameters set by the sampling personnel. The unit has sufficient memory to store 3600 data points and can record H_2S gas concentrations at intervals of 1 s to 5 min. Recording data at 5-min interval allows for 12.5 days of continuous data collection.

The STX70 and TMX412 are programmed using a personal computer to record H_2S gas samples at specified time intervals. Typically, data loggers are programmed for 2 minutes, which allows for a total of 5 d. The hydrogen sulfide gas monitoring station is secured tightly with rope so that it hangs inside the manholes without coming into contact with wastewater. The gas detectors should be calibrated according to the manufacturers

recommended schedule using manufacturer supplied equipment and NBS traceable calibration gas.

Wastewater Sampling

Sensidyne Model 211L and 211LL Gastec (or equal) tubes can be used to determine dissolved sulfide concentrations in wastewater. Gastec tubes draw wastewater by capillary forces through an indicator compound that reacts with the dissolved sulfide ions and changes from white to light brown color. The range of sulfide measurements on the 211L and 211LL Gastec tubes is 0 to 100 ppm and 0.5 to 20 ppm, respectively. This type of detection tube can be performed within one minute on freshly collected samples. Immediate field-testing is required because the sulfide ion is very unstable; it is easily stripped from solution and is easily oxidized by bacteria and available electron acceptors. The alternative wet chemical methods require that each sample be preserved and transported to a lab for testing. Both of these actions artificially lower the dissolved sulfide concentration. Also, the tubes can be carried into the sewer by the project engineer. Liquid grab samples are collected in 2 in. diameter by 3 in. tall sampling containers lowered to the water surface. The sample is retrieved and immediately tested for dissolved sulfide concentration. For quality assurance (QA), duplicate measurements are needed every 10 samples with at least one duplicate sample per day. The QA objective for 211L is +/- 15% (or 0.5 mg/L). The QA objective for 211LL is +/- 15% (or < 0.25 mg/L). If duplicate samples are not within the QA objective run duplicate samples for the next 3 samples. If duplicate samples continue not to be within the QA objective, suspend sampling and contact the manufacturer.

Pore Space Sampling

Liquid samples from within the matrix of the debris layers in the sewer will be collected using a new sampling apparatus. The apparatus consists of a stainless steel sampling cylinder with an O-ring seat for a Gastec tube and a sample collection nozzle that consists of a cylinder with perforated walls and a stainless steel screen filter inside. The entire apparatus is inserted into the debris layer. The cylinder has perforated walls and a stainless steel screen filter inside. Small debris and water from the void spaces in the debris layer passes through the holes in the cylinder to the interior screen, which removes the debris and allows water to accumulate for analysis. The driving force is the pressure differential between the water surface and the sample nozzle in the debris. The device can also be equipped with a 5 mL syringe to provide additional suction if needed.

Continuous Dissolved Sulfide Sampling

American Sigma Streamline model 800SL automatic portable liquid samplers (or equal) should be used to collect wastewater samples over a 24-hour period at each desired sampling location. The sampler contains 24 - 575 mL plastic bottles that can be programmed to collect one 100 mL sample per hour. The ends of the Gastec 211LL (or 211L) tube can be broken off and then inserted into each bottle when the sampler is set up (blue end up). As each bottle is filled, the sulfide reaction and color change occurs. When the sampler is opened the following day, the dissolved sulfide measurements are read directly off of the scale on the side of the tube. The bottles are cleaned and re-loaded with fresh Gastec tubes and another day of sampling continues. The sampler can be moved to another location or left in the same location for additional data collection.

Collecting three samples and testing for dissolved sulfide will confirm the consistency of the continuous sampling data. The tubes will be read at time zero and read again after 24 hours. Quality assurance and quality control (QA/QC) from previous continuous sampling projects indicate a change of less than 5% over 24 hours. It is understood that wastewater streams are different. If the test concentration varies by more than 0.5 mg/L, then the continuous sampling period will be reduced to a length of time that is within the stated limits.